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FUEL OIL COMPOSITIONS

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FUEL OIL COMPOSITIONS

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Claims

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1. Fuel oil compositions containing (A) a middle distillate containing 0.2 wt% or less sulfur and 40 wt% or less aromatic compounds and (B) a C₈₋₃₀ fatty acid mixture containing at least 75 wt% unsaturated fatty acids ((a) unsaturated fatty acids with one double bond in the molecule: (b) unsaturated fatty acids with two double bonds in the molecule = 1:3 to 15:1, weight (abbreviated to "wt") ratio); the fuel compositions comprise 0.001-0.5 wt% (B) based on (A).

2. In the fuel oil compositions described in Claim 1, the unsaturated fatty acid containing one double bond in the molecule is oleic acid and the unsaturated fatty acid containing two double bonds in the molecule is linoleic acid.

* [Numbers in the right margin indicate pagination in the foreign text.]

Detailed description of the invention

[0001]

Industrial application

The present invention pertains to fuel oil compositions with improved lubricity of low-sulfur fuel oil. More precisely it pertains to fuel oil compositions with excellent lubricity for diesel engine parts.

[0002]

Prior art

Diesel engines use systems of injecting high-pressure fuel oil by fuel injection pumps, therefore heretofore wear-resistance agents have been used for reducing the wear of injection pumps. For example, as disclosed in US Patent Nos. 2252889, 4185594, 4208190 and 4204481, wear-resistance agents containing fatty acid esters, unsaturated fatty acid dimers, aliphatic primary amines or aliphatic amides of diethanolamine have been used. And as disclosed in US Patent No. 4248182 wear-resistant agents containing aliphatic monocarboxylic acids have been used as fuel oil substitutes for diesel engines.

[0003]

However, with the increase of transportation by trucks, the sulfur or aromatic compounds in gas oil (literal translation is "light oil", hereinafter the same) have a great influence on the environment. In regions such as California and Sweden, regulations have been adopted in which the sulfur and aromatic compound content is considerably limited in gas oil which participates in the release of pollutants (SO_x , NO_x , dust, and smoke) in the exhaust from diesel engines, and this trend is going to spread world-wide.

[0004]

For example, since 1985 in the state of California, USA, a law was passed to limit the allowable sulfur in gas oil to 0.05 wt% or less, furthermore since 1993 a law was added to limit the aromatic compound content to 10 wt% or less. Since the same year laws to limit the sulfur and aromatic compound content to 0.05 wt% or less and 35 wt% or less, respectively were passed one after another.

[0005]

Even in Japan in December of 1989 in the report of discussion on countermeasures for environmental pollution it was requested that the NO_x discharged from automobiles be reduced to 20-35 wt% over the short term (1993-1994) and reduced to 40-60 wt% over long term (in 10

years). For the introduction of a new technology for reducing the NO_x amount, the reduction of sulfur content is [also] requested. For this purpose a stepwise reduction of sulfur content in gas oil to 0.2 wt% in 1992 and to 0.05 wt% in 1997 was decided on.

[0006]

The reduction of sulfur and aromatic compound content in gas oil is generally carried out by catalytic hydrogenation in petroleum refining. However, the reduction of sulfur and aromatic compound content in gas oil is related to the drop of lubricity of gas oil which brings about damage to pumps and nozzles of injection devices of diesel engines.

[0007]

Up to today, for gas oil containing at least 0.2 wt% sulfur and at least 40 wt% aromatic compounds the problem related to lubricity was solved by using the aforementioned wear-resistance agents. However, in the case of gas oil containing less than 0.2 wt% sulfur and less than 40 wt% aromatic compounds, even when wear-resistance agents were used, the wear, scorch, or black smoke formation in injection pumps (particularly rotary pumps, injector nozzles, and governor sleeves) occurred or engine troubles such as unstable idle rotation and stalling of engine occurred.

[0008]

Such phenomena are largely depending on the design of engines and the shape and quality of lubricated parts, however, the improvement by lubricity-imparting agents for low-sulfur gas oil has been tried. For the lubricity-imparting agents for low-sulfur gas oil, esters and ethers were disclosed in European Patent No. 605857, Japanese Kokai Patent Application Nos. Hei 7[1995]-62363 and Hei 8[1996]-283753, and Japanese Kokoko Patent No. Hei 8[1996]-505893, however, sufficient effect has not yet been obtained for low-sulfur gas oil with poor lubricity when said esters and ethers were used.

[0009]

Problems to be solved by the invention

To improve the above-mentioned problems, this invention provides fuel oil compositions which increase the lubricity of low-sulfur middle distillates which comply with the environmental regulations and which can reduce the wear of lubricated diesel engine parts.

[0010]

Means to solve the problems

The inventors of this invention carried out a detailed study to solve the above-mentioned problems and as a result they found that lubricity was improved by adding fatty acid mixtures containing unsaturated fatty acids with specific compositions to middle distillates having low sulfur and low aromatic compound content which comply with environmental regulations, thereby they completed this invention. Namely this invention is fuel oil compositions containing 0.001-0.5 wt% (based on (A) which is middle distillates containing 0.2 wt% or less sulfur and 40 wt% or less aromatic compounds) of C₈₋₃₀ fatty acid mixtures (B) containing at least 75 wt% unsaturated fatty acids comprising 1:3 to 15:1 (weight ratio) mixture of (a) unsaturated fatty acids containing a double bond in the molecule and (b) unsaturated fatty acid containing two double bonds in the molecule.

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[0011]

Mode for carrying out the invention

The fuel oil used in this invention is low-sulfur middle distillates refined by extreme hydrogenation for complying with sulfur content regulation. The middle distillates can be obtained by distillation of petroleum and they include gasoline, kerosene, gas oil (light oil), and heavy oil and usually the boiling point is 130-400°C and ideally they are fuel oils (boiling point 180-380°C). The sulfur content of middle distillates used in this invention is 0.2 wt% or less, preferably 0.12 wt% or less, especially preferably reduced to 0.05 wt%, and furthermore the aromatic compound content is 40 wt% or less, preferably 35 wt% or less and polycyclic aromatic compound content having at least two rings is 20 wt% or less based on the middle distillates, particularly preferably the aromatic compound content is 30 wt% or less and the polycyclic aromatic compounds having at least two rings is 10 wt% or less based on the middle distillates and above all, gas oil (light oil).

[0012]

Such specific middle distillates are usually prepared by mixing straight-distilled gas oil, directly desulfurized gas oil, indirectly desulfurized gas oil, cracked gas oil, desulfurized gas oil, desulfurized kerosene, etc., followed by adjusting the sulfur and aromatic compound content to the recipe of this invention.

[0013]

The C₈₋₃₀ fatty acid mixtures used in this invention contain at least 75 wt% unsaturated fatty acids, preferably at least 85 wt% fatty acids. The unsaturated fatty acids include (1)

unsaturated fatty acids which contain one double bond in the molecule and (2) unsaturated fatty acids which contain two double bonds in the molecule and preferably C₁₂₋₂₄, more preferably C₁₆₋₂₂ fatty acids.

[0014]

Moreover, the unsaturated fatty acids in the fatty acid mixtures used in this invention contain (a) unsaturated fatty acids which contain one double bond in the fatty acid molecule and (b) unsaturated fatty acid which contain two double bonds in the fatty acid molecule, as essential fatty acids. The mixing ratio of (a) to (b) is 1:3 to 15:1 weight ratio, preferably 1:2 to 7:1, more preferably 2:3 to 2:1 in the fatty acid mixtures. The sum of fatty acid (a) and fatty acid (b) is usually at least 75 wt%, preferably at least 85 wt%.

[0015]

Examples of (a) fatty acid which contains one double bond in the fatty acid molecule include caproleic acid, undecylenic acid, myristolenic acid, palmitoleic acid, oleic acid, petroselinic acid, elaidic acid, vaccenic acid, gadoleic acid, gondoic acid, erucic acid, brassidic acid, selacholeic acid, etc. Examples of (b) fatty acid which contains two double bond in the fatty acid molecule include sorbic acid, linoleic acid, etc., and examples of unsaturated fatty acid containing at least three double bonds include eleostearic acid, linolenic acid, arachidonic acid, clupanodonic acid (sardine-oil fatty acid), herring-oil fatty acid, etc. In addition to those mentioned above, unsaturated acids such as ricinoleic acid and camlolenic acid which contain hydroxy group(s) in the molecules are also included in the examples of the above-mentioned unsaturated fatty acids.

[0016]

Among these unsaturated fatty acids, from the viewpoints of supply of starting materials and price, it is especially preferable that the unsaturated fatty acid which has one double bond in the molecule is oleic acid and the unsaturated fatty acid which has two double bonds in the molecule is linoleic acid. Other fatty acids in the fatty acid mixtures include linear saturated fatty acids and branched-chain fatty acids. Examples of the linear saturated fatty acid include caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, etc. Examples of branched-chain fatty acid include 2-ethylhexanoic acid, isononanoic acid, isotridecanoic acid, isopalmitic acid, isostearic acid, etc.

[0017]

The fatty acid mixtures used in this invention can be prepared by either mixing the above-mentioned fatty acids or by mixing the above-mentioned fatty acids with fatty acids which were derived from natural fat and oils or refined fatty acids obtained from fractionation and hydrogenation thereof. Examples of fatty acids derived from natural fat and oils include coconut oil fatty acid, palm oil fatty acid, palm kernel oil fatty acid, beef tallow fatty acid, hydrogenated beef tallow fatty acid, rape oil fatty acid, corn oil fatty acid, olive oil fatty acid, sesame oil fatty acid, soybean oil fatty acid, sunflower fatty acid, castor oil fatty acid, linseed oil fatty acid, fish oil fatty acid, hydrogenated fish oil fatty acid, tall oil fatty acid, etc.

[0018]

The suitable amount of fatty acid mixtures to be added to the fuel oil compositions of this invention is 0.001-0.5 wt%, preferably 0.002-0.1 wt%, more preferably 0.004-0.02 wt% based on the above-mentioned specific middle distillates. When the amount added is greater than 0.5 wt% the effect of the addition reach saturation and the lubricity obtained corresponding to the amount added cannot be obtained, whereas when the amount added is less than 0.001 wt% a sufficient lubricity cannot be obtained.

[0019]

In this invention, even when only fatty acid mixtures are added, the lubricity of middle distillates which comply with the environmental regulations can be obtained. For the use in cold seasons or cold districts, usually low-temperature flow improving agents are added, however, the fuel oil compositions of this invention can improve lubricity without obstructing the effect of low-temperature flow improving agents. The fatty acid mixtures of this invention can be mixed with low-temperature flow improving agents at any mixing ratio, however, the mixing ratio of the former to the latter is preferably 1:10 to 5:1.

[0020]

(Already-)known low-temperature flow improving agents can be used such as copolymers of ethylene with saturated carboxylic acid vinyl ester, ethylene-methyl methacrylate copolymer, ethylene- α -olefin copolymer, ethylene- α -olefin graft copolymer, chlorinated ethylene-vinyl acetate copolymer, ethylene-vinyl acetate-vinyl neononanoate or nanodecanoate terpolymer, polymers of unsaturated carboxylic acid alkyl esters, hydroxy group-containing nitrogen compounds and esters and partial esters or salts prepared from saturated or unsaturated fatty acids, alkylene oxide adducts of hydroxy group-containing nitrogen compounds and esters and partial esters prepared from saturated or unsaturated fatty acids (such as behenic acid diesters of

triethanolamine-ethylene oxide (1:3 molar ratio) adduct, etc.), esters and partial esters synthesized from polyhydric alcohols and saturated or unsaturated fatty acids, esters synthesized from polyoxyalkylene glycol and saturated or unsaturated fatty acids, polyhydric alcohol-alkylene oxide adducts and esters and partial esters synthesized from saturated or unsaturated fatty acids, polymers having imide/amide compounds formed from unsaturated polybasic carboxylic acids and primary amines as monomers, amide compounds and their adducts with alkylene oxide (such as ethylenediamine behenic acid diamide-propylene oxide (1:3 molar ratio) adduct, etc.), phosphoric acid or phosphorus acid and esters of their adducts with alkylene oxide (such as behenic acid triester of phosphorous acid-ethylene oxide (1:3 molar ratio) adduct, etc.), alkenylsuccinic acid derivatives (such as coconut alkylamine amide/amide salt of tetrapropenylsuccinic acid, etc.), and chlorinated paraffin-naphthalene condensation products (such as Friedel-Crafts reaction products of chlorinated C₂₀₋₂₈ paraffin with naphthalene, etc.), etc. One or a combination of at least two of these low-temperature flow improving agents may be used.

[0021]

Among these additives, the use of surfactant-based low-temperature flow improving agents such as esters and partial esters synthesized from saturated or unsaturated fatty acids and hydroxy group-containing nitrogen compound-alkylene oxide adducts, esters and partial esters synthesized from saturated or unsaturated fatty acids and polyhydric alcohol-alkylene oxide adducts, etc. can impart greater lubricity, thus they are preferable.

[0022]

From the viewpoint of storage stability of the fuel oil compositions of this invention, it is preferable to add anticorrosive agents and antioxidants to the fuel oil compositions. Examples of the anticorrosive agents include partial esters formed from alcohol and dicarboxylic acids such as alkyl or alkenylsuccinic acid, etc.; ethylene oxide adducts and amidation products; polar group-containing carboxylic acids such as hydroxycarboxylic acid and mercaptocarboxylic acids; poly-acids and their derivatives of unsaturated fatty acids such as dimer acids, trimer acids; alkaline earth metal salts of fatty acid, naphthenic acid, abietic acid, alkenylsuccinic acid, thiocarboxylic acid, etc., metal salts such as magnesium salts, aluminum salts, etc., carboxylic acid amine salts, etc.; alkali metal salts of dinonylnaphthalenesulfonic acid, alkylbenzenesulfonic acid, etc., alkaline earth metal salts, sulfonic acid amine salts, etc.; partial esters formed from polyhydric alcohols such as sorbitol, glycerol, etc. and carboxylic acid such as oleic acid, etc.; higher aliphatic alcohols; morpholine, diethanolamine derivatives, amines such as rosin amine-ethylene oxide adducts, oil-soluble surfactants containing polar groups such as phosphoric

acid or boric acid as the principal or secondary polar group, etc. Among the anticorrosive agents, the preferable ones include those containing ashless ester and amino groups such as alkyl or alkenylsuccinic acid derivatives. One or a combination of at least two of these anticorrosive agents may be used.

[0023]

As the antioxidant, various antioxidants may be used which include phenol-based antioxidants such as alkylphenol, e.g., p-nonylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, tert-butylhydroxyanisole, 4,4'-methylenebis(2,3-di-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), N-butyl-p-aminophenol, hydroxyphenyl fatty acid, etc.; amine-based antioxidants such as N,N'-di-sec-butyl-p-phenylenediamine, α -naphthylamine, N-phenyl- α -naphthylamine, N,N'-disalicylidene-1,2-propylenediamine, etc.; sulfur-containing antioxidants such as alkyl ester or amine salt of laurylthiopropionic acid, alkyl ester or amine salt of carboxyethylthiosuccinic acid, etc. Among these antioxidants, preferable ones include alkylphenol, 2,4-dimethyl-6-tert-butylphenol, N,N'-di-sec-butyl-p-phenylenediamine, hydroxyphenyl fatty acids, laurylthiopropionic acid alkyl esters and amine salts. One or a combination of at least two of these antioxidants may be used.

[0024]

The fuel oil compositions of this invention can be prepared simply by adding fatty acid mixtures and if necessary the above-mentioned additives to the above-mentioned middle distillates, however, we can prepare them easier by adding to middle distillates the concentrated solutions of the fatty acids prepared by dissolving the fatty acids in organic solvents which are miscible with the middle distillates. Examples of such organic solvents include fractions of distillates of petroleum such as naphtha, kerosene, gas oil; aromatic hydrocarbons, paraffin hydrocarbons, etc. In case of diluting with organic solvents, it is preferable to use organic solvents containing 20-80, more preferably 35-75 wt% additives.

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[0025]

There is no limitation to the methods for compounding the fatty acid mixtures with various additives, however, in case of compounding low-temperature flow improving agents, it is preferable to dissolve the fatty acid mixtures and the low-temperature flow improving agents, respectively in suitable solvents, followed by adding them to the middle distillates. It is preferable that the anticorrosive agents and the antioxidants are mixed with the fatty acid mixtures, followed by adding to the middle distillates. Furthermore, to the fuel oil compositions

of this invention, additives which are usually added to fuel oil such as clouding point-dropping agents, cetane number improving agents, metal deactivators, detergent dispersants, combustibility improving agents, black smoke reducing agents, antifoaming agents, hue stabilizers, antifreezers, sludge dispensing agents, markers, etc. may be jointly used.

[0026]

Application examples

In the following, application examples will be used to explain this invention in more detail.

[0027]

Application Examples 1-15

The fuel oil compositions of this invention were prepared by compounding the middle distillates shown Table 3 with the fatty acid mixtures shown in Table 4 and the following additives (anticorrosive agents and low-temperature flow improving agents) having the proportions shown in Tables 1 and 2.

[0028]

Anticorrosive agents

B-1: Tetrapropylenylsuccinic acid propylene glycol ester

B-2: Oleic acid aminoethylethanolamine salt

Antioxidants

C-1: 2,6-Di-tert-butyl-p-cresol

C-2: 4-Nonylphenol

C-3: N,N'-di-sec-butyl-p-phenylenediamine

Low-temperature flow improving agents

D-1: ECA8400 (Exxon Chemical Japan Ltd.)

D-2: Sunhib S101 (Nippon Oil & Fats Co., Ltd.)

[0029]

Table 1

① 実施例番号	1	2	3	4	5	6	7	8
② 中間留出油	E-1	E-1	E-2	E-2	E-2	E-2	E-2	E-2
③ 脂肪酸混合物 添加量 (重量%) [*]	A-4 0.015	A-5 0.015	A-1 0.01	A-1 0.0075	A-1 0.01	A-2 0.01	A-3 0.01	A-4 0.01
④ 防錆剤 添加量 (重量%) [*]	B-1 0.001	B-2 0.002	—	B-1 0.0005	B-1 0.0005	—	—	—
⑤ 酸化防止剤 添加量 (重量%) [*]	C-2 0.005	—	C-3 0.0025	—	—	C-1 0.003	—	—
⑥ 低温流動性向上剤 添加量 (重量%) [*]	D-2 0.01	D-1 0.01	—	—	—	—	—	—
⑦ 註) * : 中間留出油に対する重量%								

- Key: 1 Application Example No.
 2 Middle distillate
 3 Fatty acid mixture amount added (wt%)*
 4 Anticorrosive agent amount added (wt%)*
 5 Antioxidant amount added (wt%)*
 6 Low-temperature flow improving agent amount added (wt%)*
 7 Notes) *: wt% based on middle distillate

[0030]

Table 2

① 実施例番号	9	10	11	12	13	14	15
② 中間留出油	E-2	E-2	E-2	E-2	E-2	E-2	E-3
③ 脂肪酸混合物 添加量 (重量%) [*]	A-4 0.01	A-4 0.005	A-4 0.01	A-5 0.005	A-5 0.01	A-5 0.01	A-4 0.0025
④ 防錆剤 添加量 (重量%) [*]	B-1 0.0005	B-1 0.0005	B-1 0.0005	B-2 0.001	B-2 0.001	—	B-1 0.0005
⑤ 酸化防止剤 添加量 (重量%) [*]	C-2 0.002	C-2 0.002	C-2 0.0025	—	—	C-3 0.0015	C-2 0.002
⑥ 低温流動性向上剤 添加量 (重量%) [*]	D-1 0.03	D-2 0.025	D-2 0.025	D-2 0.025	D-2 0.025	—	D-2 0.025
⑦ 註) * : 中間留出油に対する重量%							

- Key: 1 Application Example No.
 2 Middle distillate
 3 Fatty acid mixture amount added (wt%)*
 4 Anticorrosive agent amount added (wt%)*
 5 Antioxidant amount added (wt%)*
 6 Low-temperature flow improving agent amount added (wt%)*

7 Note) *: wt% based on middle distillate

[0031]

Table 3

①	中間留出油	E-1	E-2	E-3
②	硫黄分 (重量%)	0.006	0.032	0.13
③	芳香族分 (重量%)	7	15	28
	IBP (°C)	165	218	183
	EP (°C)	281	353	371
	ΔT(90-10) (°C)	66	72	131

④ 註)
 IBP : 中間留出油の初留点
 EP : 中間留出油の留出終点温度
 ΔT(90-10) : 90wt%留出温度と10wt%留出温度との差

Key: 1 Middle distillate
 2 Sulfur content (wt%)
 3 Aromatic compound content (wt%)
 4 Notes) IBP: Initial cut temperature
 EP: end cut temperature
 ΔT(90-10): difference between 90 wt% distillate temperature and 10 wt% distillate temperature

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[0032]

Table 4

①	飽和脂肪酸(%)		不飽和脂肪酸(%) ②			不飽和脂肪酸含量(%)	C ₁₈ :F ₁ /C ₁₈ :F ₂ (重量比) ④
	C ₁₈	C ₁₈	C ₁₈ :F ₁	C ₁₈ :F ₂	C ₁₈ :F ₂		
A-1	4	1	85	8	2	95	11/1
A-2	23	-	64	10	3	77	6/1
A-3	12	5	38	40	8	83	1/1
A-4	4	1	43	43	9	95	1/1
A-5	1	1	31	46	20	98	2/3

⑤ 註)
 C₁₈ : 高純度パルミチン酸 (パルミチン酸 99.3 重量%)
 C₁₈ : 高純度ステアリン酸 (ステアリン酸 99.1 重量%)
 C₁₈:F₁ : 高純度オレイン酸 (日本油脂 (株) 製 EXTRA OLEIC 99、オレイン酸 99.6 重量%)
 C₁₈:F₂ : 高純度リノール酸 (日本油脂 (株) 製 EXTRA LINOLEIC 99、リノール酸 99.3 重量%)
 C₁₈:F₃ : 高純度リノレイン酸 (日本油脂 (株) 製 EXTRA γ-LINOLEIC 99、γ-リノレイン酸 99.1 重量%)
 % : 脂肪酸混合物中の重量%

- Key: 1 Saturated fatty acid (%)
 2 Unsaturated fatty acid (%)
 3 Unsaturated fatty acid content (%)
 4 $C_{18}: F_1/C_{18}: F_2$ (wt ratio)
 5 Notes) C_{16} : high-purity palmitic acid (palmitic acid 99.3 wt%)
 C_{18} : high-purity stearic acid (stearic acid 99.1 wt%)
 $C_{18}: F_1$: high-purity oleic acid (Extra Oleic 99, oleic acid 99.6 wt%, Nippon Oil & Fats Co., Ltd.)
 $C_{18}: F_2$: high-purity linoleic acid (Extra Linoleic 99, linoleic acid 99.3 wt%, Nippon Oil & Fats Co., Ltd.)
 $C_{18}: F_3$: high-purity linolenic acid (Extra γ -Linolenic 99, γ -linolenic acid 99.1 wt%, Nippon Oil & Fats Co., Ltd.)
 % : wt% in fatty acid mixture

[0033]

The lubricity of the thus obtained fuel oil compositions was evaluated by using a lubrication abrasion tester. For the lubrication abrasion tester, a vibrational friction abrasion tester was used. (HFRR tester). As the specimen, Φ 10 mm, thickness 3.0 mm disk and Φ 6 mm bearing ball (PCS Instruments Co.) were used. A specified amount of the above-mentioned additives were added to the aforementioned low-sulfur gas oil and then the lubricity was measured under the following conditions.

[0034]

Tester: HFR2 (Ver. 3.0, PCS Instruments Co.)
 Specimen material: both disk and ball were steel AISI E-52100
 Temperature (°C): 60 ± 2
 Amplitude (mm): 1.0 ± 0.03
 Amount of specimen (mL): 2.0 ± 0.20
 Operating time (minutes): 75 ± 0.1
 Load (g): 200 ± 1
 Frequency (Hz): 50 ± 1
 Surface area of specimen (cm²): 6 ± 1

[0035]

The diameters of the abrasion (wear) marks of the upper ball in the oscillatory direction and orthogonal direction were measured by a microscope to calculate the average diameter of the

abrasion marks. Furthermore it was classified into the following four steps according to the shape of the abrasion marks.

Shape of abrasion marks

Shallow streaky marks to the oscillatory direction can be seen ----- *

Some deep streaky abrasion can be seen ----- **

Some aggregated abrasion (wear) and abrasive wear can be seen ----- ***

Aggregated abrasion and abrasive wear can be seen in the whole area ----- ****

[0036]

From the average diameter and shape of the wear (abrasion) marks, a comprehensive evaluation shown in Table 5 was carried out.

[0037]

Table 5

①	②	③	④
①	②	③	④
0. 3 2 5 未満 ④	② *	◎	
0. 3 2 5 未満 ④	**	◎	
0. 3 2 5 ~ 0. 4 0 0	*	○	
0. 3 2 5 ~ 0. 4 0 0	**	○	
0. 3 2 5 ~ 0. 4 0 0	***	△	
0. 4 0 0 ~ 0. 4 5 0	**	△	
0. 4 0 0 ~ 0. 4 5 0	***	×	
0. 4 5 0 以上 ⑤	***	×	
0. 4 5 0 以上 ⑤	****	×	

Key: 1 Average diameter of wear marks (mm)
 2 Shape of wear marks
 3 Comprehensive evaluation
 4 Less than _____
 5 Greater than _____

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[0038]

Further, as to the compositions of Application Examples 1, 2, 9-13, and 15 containing low-temperature flow improving agents, for the evaluation of the low-temperature property the cold filter plugging point (CFPP) was measured in accordance with the regulation of JIS K-2288 and the results are shown in Table 6.

[0039]

Table 6

④

①	摩耗痕の平均径 (mm)	② 摩耗痕の形状	③ 総合評価	CFPP (°C)
実施例 1	0. 3 6 3	**	○	- 2 3
実施例 2	0. 3 9 8	**	○	- 2 6
実施例 3	0. 3 4 2	**	○	
実施例 4	0. 3 7 0	**	○	
実施例 5	0. 3 2 8	**	○	
実施例 6	0. 3 4 8	**	○	
実施例 7	0. 3 2 1	*	◎	
実施例 8	0. 2 9 5	*	◎	
実施例 9	0. 3 0 1	*	◎	- 4
実施例 10	0. 2 9 7	**	◎	- 8
実施例 11	0. 2 5 8	*	◎	- 8
実施例 12	0. 3 3 3	**	○	- 8
実施例 13	0. 2 8 4	*	◎	- 4
実施例 14	0. 3 1 7	**	◎	
実施例 15	0. 3 6 5	*	◎	- 7

Key: 1 Average diameter of wear marks (mm)
 2 Shape of wear marks
 3 Comprehensive evaluation
 4 Application Example _____

[0040]

Comparative Example 1

For the middle distillates shown in Table 3, as in Application Example 1 the average diameter of the wear marks was measured, the shape of the wear marks was observed and comprehensive evaluation was carried out. Further, CFPP was measured as in Application Example 1 and the results are shown in Table 7.

[0041]

Table 7

(1) 中間留出油	(2) 摩耗痕の 平均径 (mm)	(3) 摩耗痕の形状	(4) 総合 評価	CFPP (°C)
E-1	0. 6 8 8	*****	×	-19
E-2	0. 5 8 5	*****	×	-1
E-3	0. 4 8 1	*****	×	+1

Key: 1 Middle distillate
 2 Average diameter of wear marks
 3 Shape of wear marks
 4 Comprehensive evaluation

[0042]

Comparative Examples 2-7

As shown in Table 8, fuel oil compositions were prepared by adding well-known lubricating agents to the middle distillates. As in Application Example 1 the average diameter of the wear marks was measured and the shape of the wear marks was observed and then comprehensive evaluation was carried out. The results are shown in Table 8.

[0043]

Table 8

	(1) 中間留出油	(2) 潤滑油	添加量 (重量%) (3)	(4) 摩耗痕の 平均径 (mm)	(5) 摩耗痕の 形状	(6) 総合 評価
比較例 2	E-1	ToA	0.015	0. 5 1 3	*****	×
比較例 3	E-2	ToA	0.01	0. 4 1 9	*****	×
比較例 4	E-2	ExO	0.01	0. 3 7 0	*****	△
比較例 5	E-2	ExL	0.01	0. 3 8 8	*****	△
比較例 6	E-2	G10	0.01	0. 3 5 5	*****	△
比較例 7	E-3	ToA	0.0025	0. 4 3 5	*****	×

(7) {

(8) { 註)
 ToA..... トール油脂肪酸重合物 (モノマー酸: ダイマー酸: トリマー酸=8:74:18、重量比)
 ExO..... 高純度オレイン酸 (日本油脂 (株) 製 EXTRA OLEIC99、オレイン酸99.6重量%)
 ExL..... 高純度リノール酸 (日本油脂 (株) 製 EXTRA LINOLEIC99、リノール酸99.8重量%)
 G10..... グリセリンオレイン酸ジエステル

Key: 1 Middle distillate
 2 Lubricating oil
 3 Amount added(wt%)*

- 4 Average diameter of wear mark (mm)
- 5 Shape of wear mark
- 6 Comprehensive evaluation
- 7 Comparative Example
- 8 Notes) ToA-----Tall oil fatty acid polymer (monomer acids: dimer acids: trimer acids = 8: 74: 18, weight ratio)
ExO-----High-purity oleic acid (Extra Oleic 99, oleic acid 99.6 wt%, Nippon Oil & Fats Co., Ltd.)
ExL-----High-purity linoleic acid (Extra Linoleic 99, linoleic acid 99.3 wt%, Nippon Oil & Fats Co., Ltd.)
G10-----Glucero1 oleic acid diester

[0044]

From the results of Tables 6-8 we can see that while the fuel oil compositions of this invention use low-sulfur middle distillates, they are excellent in lubricity, and in case the compositions contain low-temperature flow improving agents, the low-temperature property (performance) of the low-temperature flow improving agents is not impaired. Furthermore when surfactant-based low-temperature flow improving agents are combined, the lubricity imparting effect is large as well.

[0045]

Effect of the invention

The fuel oil compositions of this invention increase the lubricity of low-sulfur middle distillates which comply with environmental regulations and reduce the wear of lubricated diesel engine parts. Furthermore in case the compositions contain low-temperature flow improving agents, the low-temperature property (performance) of the low-temperature flow improving agents is not impaired.